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(19)



(54) POLYBLENDS

(71) We, THE B.F. GOODRICH COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 277 Park Avenue, New York, State of New York 10017, United States of America, (assignee of DONALD GLENN FRAZER, PHILIP HUBERT STARMER and MARTIN EDWARD WOODS), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to polyblends. It is well known that vinyl resins may be plasticized i.e. changed from a hard, horny and stiff state to a soft, plastic, workable condition, by the addition at elevated temperatures of certain plasticizers, such as dioctyl phthalate. Also, it is well known that vinyl resins may be converted into resilient, resistant rubber-like compositions by blending in a conventional mixing machine of the type normally used for mixing rubber or plastics, for example a roll mill or a Banbury mixer, with a synthetic rubber copolymer of butadiene-1,3 and acrylonitrile. Compositions of this type are referred to as "polyblends" and normally have a plasticizer for the vinyl resin incorporated therein. However, these compositions must be fluxed, i.e. heated to a predetermined temperature during mixing, in order to sufficiently soften the vinyl resin. This is time consuming and expensive.

An alternative method of making the polyblends comprises blending a rubber copolymer latex, such as one of butadiene-1,3 and acrylonitrile, with a vinyl resin latex and a plasticizer emulsion; this method has utility since many uses for blends containing a nitrile rubber latex and a resinous vinyl latex have been developed for example in coating fabric, particularly the underside of fabric of floor covering materials, such as carpeting, to provide reinforcement. However, there are problems inherent in this method in that the plasticizer softens the nitrile rubber latex during the drying stage but does not, to any

satisfactory extent, soften the vinyl resin latex during the drying stage. As a result, the polyblend is sticky and difficult to handle. To avoid this undesirable phenomenon it is necessary to have a significant proportion of the plasticizer in more intimate contact with the vinyl resin. Thus, it can be seen that a process which would enable direction of the plasticizer to the vinyl resin portion of the polyblend would be most desirable and beneficial.

We have unexpectedly found that plasticized polyblends comprising nitrile rubber and vinyl resin can be prepared without the use of strenuous mixing and shearing action at high temperatures by employing a vinyl resin which has been prepared by a procedure which comprises polymerizing the monomer in the presence of a plasticizer for vinyl resins, the plasticizer being one that is compatible with the nitrile rubber employed in the polyblend. This type of polymerization is referred to hereinafter as "plastimerization".

According to the present invention there is provided a plasticized polyblend which comprises (a) a nitrile rubber (b) a vinyl resin which has been prepared by a procedure which comprises polymerizing a monomer which is a vinyl halide or a vinylidene halide or a mixture of a vinyl halide and a vinylidene halide or a mixture of a vinyl or vinylidene halide with at least one other vinylidene monomer polymerizable therewith and having at least one terminal $\text{CH}_2=\text{Q}<$ grouping in the presence of up to 100 parts by weight, per hundred parts by weight of monomer, of a plasticizer for the vinyl resin, and (c) plasticizer for the vinyl resin, the plasticizer being compatible with the nitrile rubber and at least part of the plasticizer content of the polyblend being that plasticizer which was present during polymerization of said monomer.

According to the present invention there is also provided a process for making a plasticized polyblend according to claim 1 which comprises (1) polymerizing a monomer which is a vinyl halide or a vinylidene halide or a mixture of a vinyl and a vinylidene halide or

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a mixture of a vinyl or vinylidene halide and at least one other vinylidene monomer polymerizable therewith and having at least one terminal $\text{CH}_2=\text{C}<$ grouping in an aqueous medium containing a polymerization initiator and up to 100 parts by weight, per hundred parts by weight of monomer, of a plasticizer for the resultant polymer, (2) mixing the resultant polymer-containing aqueous medium with a nitrile rubber latex containing a copolymer of a butadiene-1,3 hydrocarbon (as hereinafter defined) and an acrylic nitrile and an aqueous emulsion containing stabilizer and (3) mixing the resultant blend with a water-soluble coagulating agent thereby to coagulate the emulsified material present in the blend. Preferred vinyl or vinylidene monomer is vinyl chloride or vinylidene chloride or a mixture of vinyl chloride or vinylidene chloride and at least one other said vinylidene monomer wherein said at least one other vinylidene monomer constitutes not more than 80% by weight of the mixture.

In the present specification the term "vinyl resin" means homopolymers and copolymers of vinyl and vinylidene halides, such as vinyl chloride and vinylidene chloride i.e. the vinyl resin is a polyvinyl halide, a polyvinylidene halide, a copolymer of a vinyl halide and a vinylidene halide or a copolymer of a vinyl or vinylidene halide with at least one other vinylidene monomer copolymerizable therewith and having at least one terminal $\text{CH}_2=\text{C}<$ grouping. Examples of such vinylidene monomers are α,β -olefinically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, ethacrylic acid, α -chloroacrylic acid, and α -cyanoacrylic acid; esters of acrylic acid such as methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate and cyanoethyl acrylate; esters of methacrylic acid such as methyl methacrylate and butyl methacrylate; nitriles such as acrylonitrile and methacrylonitrile, acrylamides such as methyl acrylamide, N-methylol acrylamide and N-butoxy methacrylamide; vinyl ethers such as ethyl vinyl ether and chloroethyl vinyl ether; vinyl ketones such as methyl vinyl ketone, styrene and styrene derivatives such as chlorostyrene and α -methyl styrene; vinyl toluene; vinyl naphthalene, vinyl acetate; vinyl chloroacetate; allyl chloroacetate; vinyl pyridine; di-olefins such as butadiene, isoprene and chloroprene; mixtures of any of these monomers and other vinylidene monomers copolymerizable therewith such as esters of maleic and fumaric acid; and other vinylidene monomers of the types known to those skilled in the art. The present invention is particularly applicable to the use of a vinyl resin which has been prepared from monomer which is vinyl chloride or vinylidene chloride or a mixture of vinyl chloride or vinylidene chloride and at least one other vinylidene monomer wherein the at least one other vinylidene mono-

mer constitutes not more than 80% by weight of the mixture. The most preferred vinyl resin is polyvinyl chloride and the invention hereinafter will be described in connection therewith, it being understood that this is merely intended in an illustrative sense and not limitative.

The nitrile rubber is a copolymer of a butadiene-1,3 hydrocarbon, by which is meant butadiene-1,3 or a homolog thereof, such as isoprene, and an acrylic nitrile, such as acrylonitrile or methacrylonitrile. The preferred nitrile rubber is a copolymer of butadiene-1,3 and acrylonitrile. The nitrile rubber may be prepared by any of the known methods of preparing copolymers, although it has been found that nitrile rubbers prepared by emulsion polymerization give the best results, particularly when the polyblend is prepared using a nitrile rubber latex, as will be described hereinafter. The nitrile rubber may contain other material in small amounts either in copolymerized form with the butadiene-1,3 hydrocarbon and the acrylic nitrile or in the form of post-polymerization additive. It is desirable that the nitrile rubber be rendered as plastic as is consistent with high ultimate strength by mastication or by any other means, such as by the addition thereto of a plasticizer for example, before use in forming the polyblend of the present invention. The preferred nitrile rubber is a copolymer of 50 to 80% by weight of a butadiene-1,3 hydrocarbon and 50 to 20% by weight of an acrylic nitrile since copolymers of this composition are more compatible with the polyvinyl resin, although copolymers having a higher butadiene content may be employed.

While the vinyl resin may be prepared by any of the usual polymerization techniques, it is preferably prepared by an emulsion polymerization technique in an aqueous medium. Plasticizers suitable for use in the polymerization reaction are the organic phosphoric esters, such as tricresyl phosphate, triphenyl phosphate and isodecyl diphenyl phosphate, and the phthalic esters, such as dioctyl phthalate, dimethyl phthalate, dibutyl phthalate, dilauryl phthalate, dimethyl tetrachlorophthalate and butyl phthalyl butyl glycolate, although any known plasticizer for polymeric vinyl halides may be employed in the polymerization reaction. It has been found that the maximum amount of plasticizer that can be used in the polymerization reaction is 100 parts by weight per hundred parts by weight of monomer. When a larger amount of plasticizer is used, the polymerization rate and the degree of conversion are adversely affected.

When the vinyl resin is prepared by an emulsion polymerization technique, the aqueous medium may be emulsifier-free or may contain an emulsifier. Suitable emulsifiers are the general types of anionic and

nonionic emulsifiers. Excellent results have been obtained using anionic emulsifiers. Useful anionic emulsifiers include alkali metal and ammonium salts of the sulfates of alcohols having from 8 to 18 carbon atoms, such as sodium lauryl sulfate, ethanolamine lauryl sulfate and ethylamine lauryl sulfate; alkali metal and ammonium salts of sulfonated petroleum and paraffin oils; sodium salts of aromatic sulfonic acids, such as dodecane-1-sulfonic acid and octadiene-1-sulfonic acid; aralkyl sulfonates, such as sodium isopropyl benzene sulfonate, sodium dodecyl benzene sulfonate and sodium isobutyl naphthalene sulfonate; alkali metal and ammonium salts of sulfonated dicarboxylic acid esters, such as sodium dioctyl sulfosuccinate and disodium-n-octadecyl sulfosuccinamate; alkali metal and ammonium salts of free acid of complex organic mono- and di-phosphate esters. Useful nonionic emulsifiers include octylphenyl- and nonylphenyl-polyethoxyethanol. Vinyl resin latices having excellent stability are obtained employing the alkali metal and ammonium salts of aromatic sulfonic acids, aralkyl sulfonates and long chain sulfonates.

The emulsifier may be used in an amount up to 6% based on the weight of monomer being polymerized, although amounts of more than 6% may also be used. The emulsifier may be added all at once at the start of the polymerization reaction or incrementally or continuously throughout the reaction.

Polymerization is preferably conducted at a temperature of from 20°C. to 70°C. in the presence of a compound capable of initiating the polymerization reaction. Free radical initiators are commonly used. Suitable free radical initiators are, for example, peroxygen compounds, such as persulfates, benzoyl peroxide, t-butyl hydroperoxide, cumene hydroperoxide, t-butyl di-perphthalate, pelargonyl peroxide and 1-hydroxycyclohexyl hydroperoxide; and azo compounds, such as azodiisobutyl-nitrile and dimethylazodiisobutyrate. Particularly useful initiators are water-soluble peroxygen compounds, such as hydrogen peroxide and sodium, potassium and ammonium persulfates used alone or as part of an activated redox system. Suitable redox systems are those which comprise an alkali metal persulfate in combination with a reducing agent, for example, sodium sulfite, sodium bisulfite, a reducing sugar, dimethylamino propionitrile, a diazomercapto compound or a water-soluble ferricyanide compound. Heavy metal ions may also be used to activate persulfate catalyzed polymerization. Particularly useful initiators are alkali metal and ammonium persulfate. The amount of initiator used will be generally between 0.1% and 3.0% by weight, preferably between 0.15% and 1.0% by weight, based on the weight of monomer. The initiator may be charged all at once at the outset of the polymerization.

However, it is often advantageous to employ incremental or continuous addition of the initiator throughout the polymerization.

While the pH at which polymerization is effected is not critical it is preferred that a pH of 7 or below be maintained during the polymerization. This is accomplished by employing buffering agents such as trisodium phosphate and tetrasodium pyrophosphate.

The vinyl resin latex produced may subsequently be adjusted to any desired pH. When the polyblend is prepared using plastimerized vinyl resin as in the present invention it is possible for the polyblend to contain a relatively greater amount of plasticizer for example from 5 to 100 parts by weight per hundred parts by weight of total polymer. This includes both the plasticizer present in the plastimerized polymer and any plasticizer present in the emulsion containing stabilizer. The emulsion containing stabilizer is made by any of the usual emulsion preparation techniques which are well known to those skilled in the art and may additionally contain plasticizer if extra plasticizer is required to achieve the desired final plasticizer content of the polyblend.

The plastimerized vinyl resin latex, the nitrile rubber latex and the plasticizer-stabilizer or stabilizer emulsion, may be blended together, for example by stirring, in relative amounts such that the blend contains, per 100 parts by weight of nitrile rubber and plastimerized vinyl resin latices, from 10 to 90 parts by weight of the nitrile rubber latex and from 90 to 10 parts by weight of the plastimerized vinyl resin latex. This blending can be conveniently carried out at room temperature in any suitable vessel equipped with a suitable stirring means. Thereafter, the emulsified material present in the blend is coagulated by mixing the blend with a suitable coagulating agent, for example, by pouring the blend into an aqueous solution of a water-soluble coagulating agent. The most suitable coagulating medium is an aqueous solution of calcium chloride, for example a solution having a concentration of calcium chloride of 3% to 10% by weight. Another water-soluble coagulating agent may be employed, such as a water-soluble metal sulfate or chloride, for example, sodium chloride, barium chloride, aluminum sulfate or magnesium sulfate. The resulting polyblend is then separated from the aqueous medium. For example, the coagulated polyblend may be separated from the aqueous medium by filtering, washing with soft water (demineralized water), and drying, for example, in conventional equipment, such as a drying oven or Fourdrinier apparatus.

Heretofore the production of highly plasticized vinyl resin and nitrile rubber polyblends, made via latex blending, was impeded by the fact that the blends were too sticky to dry in conventional equipment. As pointed

out above, the stickiness was due to the presence of most of the plasticizer in the nitrile rubber phase of the blend. In the polyblends of the present invention, wherein plastimerized vinyl resins are employed, stickiness is no longer a problem, because the ratio of plasticizer nitrile rubber phase to plasticizer in the vinyl resin phase is sufficiently low to prevent stickiness. Also, as a result of this lack of stickiness, the polyblends of the present invention can be extrusion dried.

To further illustrate the present invention, the following specific examples are given, it being understood that this is merely intended in an illustrative and not a limitative sense. In the examples all parts and percents are by weight unless otherwise indicated.

EXAMPLE I.

This Example illustrates the preparation of a nitrile rubber latex made from butadiene-1,3 and acrylonitrile.

A copolymer was prepared in the form of a latex by emulsion polymerization at 5°C. according to the following recipe:

Material	Parts
Butadiene-1,3	74.7
Acrylonitrile	35.6
Emulsifier ⁽¹⁾	4.6
Dispersant ⁽²⁾	0.1
Sodium formaldehyde sulfoxylate	0.1
Cumene hydroperoxide	0.12
Sequestered iron	0.008
Soft water	195.0

⁽¹⁾Sodium salt of abiatic acid.

⁽²⁾A polymerized sodium salt of an alkyl naphthalene sulfonic acid.

The polymerization reaction was continued until 85% of the monomeric material had been converted to the copolymer the reaction being stopped by the use of the shortstopping agent hydroxyl ammonium sulfate (0.42 part). The latex thus produced had a total solids content of 30%.

EXAMPLE II.

This Example illustrates the preparation of plastimerized vinyl chloride latex.

A first plastimerized polyvinyl chloride latex was prepared by emulsion polymerization at 45°C. according to the following recipe:

Material	Parts
Soft water	200
Vinyl chloride	100
Di-octyl phthalate	90
Sodium lauryl sulfate	0.9
Isopropyl percarbonate	0.1

The polymerization reaction was continued until 75% of the monomer had been con-

verted to polyvinyl chloride. The latex thus produced had a total solids content of 37.5%. This latex is designated Ex. II for subsequent identification.

A second plastimerized polyvinyl chloride latex was prepared using the above recipe and polymerization conditions except that only 63 parts of di-octyl phthalate were employed. The latex so produced had a total solids content of 42% and is designated Ex. II—A for subsequent identification.

EXAMPLE III.

A blend of latices, for purposes of a polyblend control, was prepared as follows: 2312 grams of the latex prepared in Example I were blended, at a pH of 10, with agitation, with 1864 grams of a polyvinyl chloride latex, made in the absence of plasticizer by a standard emulsion polymerization reaction to give 38% total solids in the latex. Thereafter the blend of latices was added to a plasticizer-stabilizer emulsion which was made by homogenizing the following ingredients:

Soft water	1000 grams
Di-octyl phthalate	960 grams
Epoxidized soybean oil	24 grams
Cadmium-barium soap	
stabilizer	12 grams
Organic phosphite	
(chelator)	4 grams
Sodium salt of dodecyl benzene sulfonate	96 grams

The emulsion thus produced was added to a solution containing 334 grams of calcium chloride in 16 pounds of soft water at 50°C. in order to coagulate the latices in the blend. When coagulation was complete, the liquid was poured off and the resulting polyblend was washed two times each time for 10 minutes using 3 gallons of soft water at a temperature of 27°—30°C. and then vacuum dried on trays. The resulting crumbs of polyblend were formed into a sheet on a standard sheet former and sheet press. The crumbs of polyblend stuck very badly to the screen, cloth and press rolls and had to be scraped off.

EXAMPLE IV.

Two blends of latices were prepared as follows: (A) 2312 grams of the latex prepared in Example I were blended, with agitation, with 2240 grams of latex Ex. II—A, at a pH of 10, and (B) 2312 grams of the latex prepared in Example I were blended, also at a pH of 10 with agitation, with 2240 grams of latex Ex. II. Thereafter, each of the blends (A) and (B) was added to a plasticizer emulsion which was made by homogenizing the following ingredients:

Soft water	496 grams
Di-octyl phthalate	456 grams

Epoxidized soybeans oil 24 grams
Cadmium-barium soap 12 grams
Sodium salt of dodecyl benzene sulfonate 4.8 grams

tested to show the superior results obtained in using a plastimerized vinyl chloride latex in the preparation of the polyblend.

Each of the polyblends was mixed on a roll mill in accordance with the following recipe:

5 Each emulsion thus produced was added to a solution containing 364.16 grams of calcium chloride in 16 pounds of soft water at 50°C. in order to coagulate the latices in the blend. When coagulation was complete, each resulting polyblend was separated from the liquid, washed and dried, in accordance with the procedure of Example III. Each of the polyblends ran well on the sheet press and there were no sticking problems, in contrast to the control blend prepared in Example III.

Materials	Parts	
Polyblend	100	
Zinc oxide	5.0	
Stearic acid	1.0	
Carbon black	40.0	30
Tetra-methyl thiuram disulfide (curing agent).	3.5	

Each resulting mixture was sheeted out in a standard sheetier and the sheets from each mixture were cured for periods of 5 minutes, 10 minutes and 20 minutes at 338°F. After curing, the sheets were tested with the following results:

EXAMPLE V.

Each of the polyblends prepared in Examples III and IV was compounded with standard materials, formed into sheets and

Vinyl chloride latex

	Cure Time	Example III	Control Ex. II	Ex. II-A
Ultimate tensile (lb. per sq. in.)	5'	1513	1673	2040
	10'	1575	1716	2143
	20'	1506	1840	2365
Ultimate elongation (percent)	5'	236	490	453
	10'	226	395	423
	20'	200	375	403
Hardness—Durometer A	5'	67	59	63
	10'	67	58	62
	20'	67	58	62

40 It can be seen, from the above results, that the polyblends of the present invention have much higher tensile strength and elongation and more, importantly, are softer than prior art polyblends of identical composition.

45 While it is preferred to form the polyblends of the present invention by blending latices of the nitrile rubber and of plastimerized vinyl resin, it is possible to blend the plastimerized vinyl resin with the nitrile rubber on a roll mill, particularly when no additional plasticizer is used when making the polyblend.

50 The polyblends have a variety of uses such as in packaging and in cable jacketing. They are particularly useful where flexibility is needed, such as in films and coatings, for example coatings on fabrics and non-woven materials. Furthermore, when non-flammable properties are desired in the end product, it is a simple matter to choose a suitable plasticizer which will result in the product having such properties. More importantly, the polyblends of the present invention are very readily

and easily transformed to finely divided powder form by standard procedure, which form provides not only ease of handling and shipping, but also economic advantages in processing by the ultimate user of fabricator.

WHAT WE CLAIM IS:—

1. A plasticized polyblend which comprises (a) a nitrile rubber (b) a vinyl resin which has been prepared by a procedure which comprises polymerizing a monomer which is a vinyl halide or a vinylidene halide or a mixture of a vinyl halide and a vinylidene halide or a mixture of a vinyl or vinylidene halide with at least one other vinylidene monomer polymerizable therewith and having at least one terminal $\text{CH}_2=\text{C}<$ grouping in the presence of up to 100 parts by weight, per hundred parts by weight of monomer, of a plasticizer for the vinyl resin, and (c) plasticizer for the vinyl resin, the plasticizer being compatible with the nitrile rubber and at least part of the plasticizer content of the polyblend being that plasticizer which was present

during polymerization of said monomer.

5 2. A polyblend as claimed in claim 1 in which the vinyl resin has been prepared from monomer which is vinyl chloride or vinylidene chloride or a mixture of vinyl chloride or vinylidene chloride and at least one other vinylidene monomer wherein at least one other vinylidene monomer constitutes not more than 80% by weight of the mixture.

10 3. A polyblend as claimed in claim 1 in which the vinyl resin is polyvinyl chloride.

4. A polyblend as claimed in any of claims 1 to 3 in which the nitrile rubber is a copolymer of butadiene-1,3 and acrylonitrile.

15 5. A polyblend as claimed in any of claims 1 to 3 in which the nitrile rubber is a copolymer of 50 to 80% by weight of a butadiene-1,3 hydrocarbon (as hereinbefore defined) and 50 to 20% by weight of an acrylic nitrile.

20 6. A polyblend as claimed in any of claims 1 to 5 in which the plasticizer is di-octyl phthalate.

25 7. A polyblend as claimed in any of claims 1 to 6 which contains plasticizer in addition to that plasticizer which was present during the polymerization of said monomer.

30 8. A polyblend according to claim 1 substantially as hereinbefore described with particular reference to the Examples.

35 9. A process for making a plasticized polyblend according to claim 1 which comprises (1) polymerizing a monomer which is a vinyl halide or a vinylidene halide or a mixture of a vinyl and a vinylidene halide and at least one other vinylidene monomer polymerizable therewith and having at least one terminal $\text{CH}_2=\text{C}<$ grouping in an aqueous medium containing a polymerization initiator and up to 100 parts by weight, per hundred parts by weight of monomer, of a plasticizer for the resultant polymer, (2) mixing the resultant polymer-containing aqueous medium

40 with a nitrile rubber latex containing a copolymer of a butadiene-1,3 hydrocarbon (as hereinbefore defined) and an acrylic nitrile and an aqueous emulsion containing stabilizer,

(3) mixing the resultant blend with a water-soluble coagulating agent thereby to coagulate the emulsified material present in the blend, and (4) separating the resultant coagulated blend from the resultant aqueous medium.

50 10. A process as claimed in claim 9 in which the monomer is vinyl chloride or vinylidene chloride or a mixture of vinyl chloride or vinylidene chloride and at least one other said vinylidene monomer wherein said at least one other vinylidene monomer constitutes not more than 80% by weight of the mixture.

55 11. A process as claimed in claim 9 in which the halide in (1) is vinyl chloride.

60 12. A process as claimed in any of claims 9 to 11 in which the nitrile rubber latex contains a copolymer of butadiene-1,3 and acrylonitrile.

65 13. A process as claimed in any of claims 9 to 11 in which the nitrile rubber of the nitrile rubber latex is a copolymer of 50 to 80% by weight of a butadiene-1,3 hydrocarbon (as hereinbefore defined) and 50 to 20% by weight of an acrylic nitrile.

70 14. A process as claimed in any of claims 9 to 13 in which the plasticizer is di-octyl phthalate.

75 15. A process as claimed in any of claims 9 to 14 in which the coagulating agent is calcium chloride.

80 16. A process as claimed in any of claims 9 to 15 in which said aqueous emulsion containing stabilizer also contains plasticizer for the vinyl resin.

85 17. A process as claimed in any of claims 9 to 16 in which, in step (4), the coagulated blend is filtered, washed with demineralized water and dried.

90 18. A process according to claim 9 substantially as hereinbefore described with particular reference to the Examples.

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